Spin Relaxation of Conduction Electrons

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Abstract

Prospect of building electronic devices in which electron spins store and transport information has revived interest in the spin relaxation of conduction electrons. Since spin-polarized currents cannot flow indefinitely, basic spin-electronic devices must be smaller than the distance electrons diffuse without losing its spin memory. Some recent experimental and theoretical effort has been devoted to the issue of modulating the spin relaxation. It has been shown, for example, that in certain materials doping, alloying, or changing dimensionality can reduce or enhance the spin relaxation by several orders of magnitude. This brief review presents these efforts in the perspective of the current understanding of the spin relaxation of conduction electrons in nonmagnetic semiconductors and metals.

I. INTRODUCTION

Electron spin is becoming increasingly popular in electronics. New devices, now generally referred to as *spintronics*, exploit the ability of conduction electrons in metals and semiconductors to carry spin polarized current. Three factors make spin of conduction electrons attractive for future technology: (1) electron spin can store information, (2) the spin (information) can be transferred as it is attached to mobile carriers, and (3) the spin (information) can be detected. In addition, the possibility of having long spin relaxation time or spin diffusion length in electronic materials makes *spintronics* a viable potential technology.

Information can be stored in a system of electron spins because these can be polarized. To represent bits, for example, spin up may stand for one, spin down for zero. But the sheer existence of two spin polarizations is of limited use if we do not have means of manipulating them. Currently used methods of polarizing electron spins include magnetic field, optical orientation, and spin injection. Polarization by magnetic field is the traditional method that works for both metals and semiconductors. Spin dynamics in semiconductors, however, is best studied by optical orientation where spin-polarized electrons and holes are created by a circularly polarized light. Finally, in the spin injection technique a spin-polarized current is driven, typically from a ferromagnet, into the metallic sample. Since spin is both introduced and transferred by current, this method is most promising for spintronics. Unfortunately, thus far spin injection has not been convincingly demonstrated in semiconductors.

The second factor, the ability of information transfer by electron spins, relies on two facts. First, electrons are mobile and second, electrons have a relatively large spin memory. Indeed, conduction electrons "remember" their spins much longer than they remember momentum states. In a typical metal, momentum coherence is lost after ten femtoseconds, while spin coherence can survive more than a nanosecond. As a result, the length L_1, the spin diffusion length, over which electrons remain spin polarized is much longer than the mean free path distance ℓ over which their momentum is lost. Since L_1 is the upper limit for the size of spintronic elements (in larger elements the spin-encoded information fades away) it is not surprising that significant effort went into finding ways of reducing the spin relaxation. Quite unexpectedly, in quantum wells, but even in bulk semiconductors, donor doping was found to increase the spin memory of conduction electrons by up to three orders of magnitude. In metals one has much less freedom in manipulating electron states. A theoretical study, however, predicts that even there spin memory can be changed by orders of magnitude by band-structure tailoring. Alloying of polyvalent metals with monovalent ones can increase the spin memory by a decade or two. The ability of conduction electrons to transport spin-polarized current over distances exceeding micrometers has now been demonstrated in both metals and semiconductors.

Finally, after the spin is transferred, it has to be detected. In many experiments the spin polarization is read optically: photoexcited spin-polarized electrons and holes in a semiconductor recombine by emitting circularly polarized light; or the electron spins interact with light and cause a rotation of the light polarization plane. It was discovered, however, that spin can be also measured electronically, through charge-spin coupling. When spin accumulates on the conductor side at the interface of a conductor and a ferromagnet, a voltage or a current appears. By measuring the polarity of the voltage or the current, one can tell the spin orientation in the conductor. Like spin injection, spin-charge coupling has

been demonstrated only in metals.

The operational synthesis of spin (information) storage, transfer, and detection can be illustrated on concrete devices. Spin transistor is a trilayer that consists of a nonmagnetic metal (base) sandwiched between two ferromagnets (emitter and collector). Spin-polarized current injected into the base from the emitter causes spin accumulation at the base-collector interface. If the collector magnetic moment is opposite to the spin polarization of the current (and parallel to the emitter magnetic moment, if the injected electrons are from the spin-minority subband), the current flows from the base into the collector. If the collector magnetic moment is parallel to the spin polarization, the current is reversed. In order for the spin accumulation to occur, the current in the metallic base must remain polarized–the base must be thinner than L_1. Similar principles work in the giant magnetoresistance effect. Multilayer structures with alternating nonmagnetic and ferromagnetic metals have their resistance strongly dependent on the relative orientation of the ferromagnetic moments. The resistance is small if the moments point in the same directions, and large if the directions of neighboring moments are reversed. Again, the information about the moment of a ferromagnetic layer is encoded into electron spins which carry this information through a contiguous nonmagnetic metal into another ferromagnet. Here the information is read and in ideal case the electron is let into the ferromagnet only if its spin is opposite to the direction of the ferromagnetic moment. Otherwise the electron is scattered at the interface.

Several recent reviews focus on spin-polarized transport. An overview of the subject can be found in [1]. Spin transistors, spin injection, and charge-spin coupling in metallic systems is treated in [2]; a comprehensive account of optical orientation is given in [3], and recent reviews of giant magnetoresistance are in [4,5]. Many suggested spintronic devices have not been demonstrated yet, but their potential seems enormous. Industrial issues related to spintronics can be found in [6,7], and [8] describes some of the recent spintronic schemes and devices.

The present article introduces basic concepts of the spin relaxation of conduction electrons and identifies important unresolved issues in both semiconductors and metals. Particular emphasis is given to the recent experimental and theoretical work that attempts to enhance and/or understand electron spin coherence in electronic materials.

II. MECHANISMS OF SPIN RELAXATION

Spin relaxation refers to the processes that bring an unbalanced population of spin states into equilibrium. If, say, spin up electrons are injected into a metal at time $t = 0$ creating a spin imbalance, at a later time, $t = T_1$ (the so called spin relaxation time), the balance is restored by a coupling between spin and orbital degrees of freedom. Three spin-relaxation mechanisms have been found to be relevant for conduction electrons (Fig. 1): the Elliott-Yafet, D'yakonov-Perel', and Bir-Aronov-Pikus.

The Elliott-Yafet mechanism is based on the fact that in real crystals Bloch states are not spin eigenstates. Indeed, the lattice ions induce the spin-orbit interaction that mixes the spin up and spin down amplitudes [9]. Usually the spin-orbit coupling λ is much smaller than a typical band width ΔE and can be treated as a perturbation. Switching the spin-orbit interaction adiabatically, an initially spin up (down) state acquires a spin down (up) component with amplitude b of order $\lambda/\Delta E$. Since b is small, the resulting states can be

still named "up" and "down" according to their largest spin component. Elliott noticed [9] that an ordinary (spin independent) interaction with impurities, boundaries, interfaces, and phonons can connect "up" with "down" electrons, leading to spin relaxation whose rate $1/T_1$ is proportional to b^2/τ (τ being the momentum relaxation time determined by "up" to "up" scattering). Additional spin-flip scattering is provided by the spin-orbit interaction of impurities, and by the phonon-modulated spin-orbit interaction of the lattice ions (Overhauser [10]). The latter should be taken together with the Elliott phonon scattering to get the correct low-temperature behavior of $1/T_1$ [11]. Yafet showed [11] that $1/T_1$ follows the temperature dependence of resistivity: $1/T_1 \sim T$ at temperatures T above the Debye temperature T_D, and $1/T_1 \sim T^5$ at very low T in clean samples (neutral impurities lead to T-independent spin relaxation). Elliott-Yafet processes due to the electron-electron scattering in semiconductors were evaluated by Boguslawski [12].

In crystals that lack inversion symmetry (such as zincblende semiconductors) the spin-orbit interaction lifts the spin degeneracy: spin up and spin down electrons have different energies even when in the same momentum state. This is equivalent to having a momentum-dependent internal magnetic field $\mathbf{B}(\mathbf{k})$ which is capable of flipping spins through the interaction term like $\mathbf{B}(\mathbf{k}) \cdot \mathbf{S}$, with $\mathbf{S}$ denoting the electron spin operator. (This term can be further modulated by strain or by interface electric fields). D'yakonov and Perel' showed that the lifting of the spin degeneracy leads to spin relaxation [13]. Typically the distance between spin up and down bands is much smaller than the frequency $1/\tau$ of ordinary scattering by impurities, boundaries, or phonons. Consider an electron with momentum $\mathbf{k}$. Its spin precesses along the axis given by $\mathbf{B}(\mathbf{k})$. Without going the full cycle, the electron scatters into momentum $\mathbf{k}'$ and begins to precess along the direction now given by $\mathbf{B}(\mathbf{k}')$, and so on. The electron spin perceives the scattering through randomly changing precession direction and frequency. The precession angle along the axis of initial polarization (or any other fixed axis) diffuses so its square becomes about $(t/\tau)(\omega\tau)^2$ after time t (ω is the typical precession frequency). By definition T_1 is the time when the precession angle becomes of order one. Then $1/T_1 \approx \omega(\omega\tau)$. The factor $(\omega\tau)$ is a result of motional narrowing as in nuclear magnetic resonance [14]. The spin relaxation *rate* $1/T_1$ is proportional to the momentum relaxation *time* τ. We note that in strong magnetic fields the precession along the randomly changing axis is suppressed (spins precess along the external field [15] and electron cyclotron motion averages over different internal magnetic fields [16,17]), leading to a reduction of the D'yakonov-Perel' spin relaxation.

Another source of spin relaxation for conduction electrons was found by Bir, Aronov, and Pikus [18] in the electron-hole exchange interaction. This interaction depends on the spins of interacting electrons and holes and acts on electron spins as some effective magnetic field. The spin relaxation takes place as electron spins precess along this field. In many cases, however, hole spins change with the rate that is much faster than the precession frequency. When that happens the effective field which is generated by the hole spins fluctuates and the precession angle about a fixed axis diffuses as in the case of the D'yakonov-Perel' process. The electron spin relaxation rate $1/T_1$ is then "motionally" reduced and is proportional to the hole spin relaxation time. Similar reduction of $1/T_1$ occurs if holes that move faster than electrons change their momentum before electron spins precess a full cycle [18]. The Bir-Aronov-Pikus spin relaxation, being based on the electron-hole interaction, is relevant only in semiconductors with a significant overlap between electron and hole wave functions.

III. SEMICONDUCTORS

Spin relaxation in semiconductors is rather complex. First, there are different charge carriers to consider. Both electrons and holes can be spin polarized and carry spin-polarized currents. Furthermore, some features of the observed luminescence polarization spectra must take into account excitons, which too, can be polarized. Second, in addition to temperature and impurity content the spin relaxation is extremely sensitive to factors like doping, dimensionality, strain, magnetic and electrical fields. The type of dopant is also important: electrons in p-type samples, for example, can relax much faster than in n-type samples. And, finally, since the relevant electron and hole states are typically very close to special symmetry points of the Brillouin zone, subtleties of the band structure often play a decisive role in determining which spin relaxation mechanism prevails. (Band structure also determines what is polarized–often due to degeneracy lifting, spin and orbital degrees are entirely mixed and the total angular momentum is what is referred to as "spin.") The above factors make sorting out different spin relaxation mechanisms a difficult task.

The first measurement of T_1 of free carriers in a semiconductor was reported in Si by Portis et al. [19] and Willenbrock and Bloembergen [20]; these measurements were done by conduction electron spin resonance. Silicon, however, remains still very poorly understood in regards to its spin transport properties. Very little is known, for example, about electronic spin-flip scattering by conventional n and p dopants. Considering that Si may be an important element for spintronics since it is widely used in conventional electronics, its spin relaxation properties should be further investigated.

Much effort was spent on III-V semiconductors where optical orientation [3] enables direct measurement of T_1. In these systems holes relax much faster than electrons because hole Bloch states are almost an equal admixture of spin up and down eigenstates. The Elliott-Yafet mechanism then gives T_1 of the same order as τ. In quantum wells (QW), however, T_1 of holes was predicted by Uenoyama and Sham [21] and Ferreira and Bastard [22] to be quenched, and even longer than the electron-hole recombination time. This was observed experimentally in n-modulation doped GaAs QWs by Damen et al. [23] who measured hole spin relaxation time of 4 ps at 10 K. Hole and exciton spin relaxation was reviewed by Sham [24].

Compared to holes, electrons in III-V systems remember their spins much longer and are therefore more important for spintronic applications. Typical measured values of electron T_1 range from 10^{-11} to 10^{-7}s. All the three spin relaxation mechanisms have been found contributing to T_1. Although it is difficult to decide which mechanism operates under the specific experimental conditions (this is because in some cases two mechanisms yield similar T_1, but also because experiments often disagree with each other [25]), some general trends are followed. The Elliott-Yafet mechanism dominates in narrow-gap semiconductors, where b^2 is quite large ($\Delta E \approx E_g$ is small). Chazalviel [26] studied n-doped InSb ($E_g \approx 0.2$ eV) and found that Elliott-Yafet scattering by ionized impurities explains the observed $1/T_1$.

If band gap is not too small, the D'yakonov-Perel' mechanism has been found relevant at high temperatures and sufficiently low densities of holes. The D'yakonov-Perel' mechanism can be quite easily distinguished from the Elliott-Yafet one: the former leads to $1/T_1 \sim \tau$ while for the latter $1/T_1 \sim 1/\tau$. The increase in the impurity concentration decreases the efficiency of the D'yakonov-Perel' processes and increases those due to Elliott and Yafet.

Another useful test of the D'yakonov-Perel' mechanism is its suppression by magnetic field [16,17]. The first experimental observation of the D'yakonov-Perel' mechanism was reported by Clark et al. on moderately doped p samples of GaAs [27] and GaAlAs [28]. Later measurements on less doped samples of GaAs by Maruschak et al. [29] and Zerrouati et al. [25] confirmed that the D'yakonov-Perel' mechanism is dominant in GaAs at elevated temperatures.

At low temperatures and in highly p-doped samples (acceptor concentration larger than 10^{17} cm^{-3}) the Bir-Aronov-Pikus mechanism prevails. As the acceptor concentration increases this mechanism reveals itself at progressively higher temperatures. An increase of $1/T_1$ with increasing p doping signals that the electron-hole spin relaxation is relevant. This was demonstrated in p-type GaAs (for example, Zerrouati et al. [25], Maruschak et al. [29], and Fishman and Lampel [30]) and GaSb (Aronov et al. [31]). The physics of spin relaxation in p-doped III-V semiconductors is very rich because several different mechanisms have been shown relevant. More work, however, still needs to be done. It is not clear, for example, what happens at very low temperatures and in very pure samples [25]. There are some indications that at very low temperatures both the D'yakonov-Perel' and the Bir-Aronov-Pikus mechanisms can explain the observed data at whatever doping [25]. Excellent reviews of conduction electron spin relaxation in bulk III-V semiconductors are [32,33]. These references contain both experimental data and many useful formulas of $1/T_1$.

Electron spin relaxation has been studied also in quantum wells. That spin dynamics in quantum wells differs from that in the bulk is obvious from the fact that the relevant spin relaxation mechanisms are very sensitive to factors like mobility (which is higher in QWs), electron-hole separation (smaller in QWs) and electronic band structure (more complicated in QWs because of subband structures and interface effects). Furthermore, the quality of QW samples is very important since $1/T_1$ is strongly influenced by localization and defects. The first measurement of conduction electron T_1 in a QW was reported by Damen et al. [23] who studied the dynamics of luminescence polarization in p-modulation doped GaAs/AlGaAs, and obtained $T_1 \approx 0.15$ ns at low temperatures. This relaxation time is three to four times smaller than in a similar bulk sample (the acceptor concentration was 4×10^{11} cm^{-2}). It was concluded [23] that the relevant mechanism was Bir-Aronov-Pikus. The recent theoretical study by Maialle and Degani [34] of the Bir-Aronov-Pikus relaxation in QWs indicates that, to the contrary, this mechanism is not efficient enough to explain the experiment. Another possibility is the D'yakonov-Perel' mechanism. Bastard and Ferreira [35] calculated the effectiveness of this mechanism for the case of ionized impurity scattering. Their calculation shows [24] that the D'yakonov-Perel' mechanism also too weak to explain the experiment. Although some assumptions of the theoretical studies may need to be reexamined (the major difficulty seems to be estimating τ) [24], further experimental work (such as temperature and doping dependence) is required to decide on the relevant mechanism. Recently Britton et al. [36] studied the spin relaxation in undoped GaAs/AlGaAs multiple quantum wells at room temperature. The measured relaxation times vary between 0.07 and 0.01 ns, decreasing strongly with increasing confinement energy. These results seem to be consistent with the D'yakonov-Perel' mechanism [36].

Spin relaxation studies in quantum wells also promise better understanding of interface effects. In an inversion layer an electric field arises from the electrostatic confinement. This field induces a spin-orbit interaction which contributes to the spin-splitting (the so called

Rashba splitting) of electron bands in addition to the inversion-asymmetry splitting. This should enhance the efficiency of the D'yakonov-Perel' mechanism. Spin precession of conduction electrons in GaAs inversion layers was investigated by Dresselhaus et al. [37] using antilocalization. The spin relaxation was found to be due to the D'yakonov-Perel' mechanism, but the spin splitting was identified (by magnetic field dependence) to be primarily due to the inversion asymmetry. This is consistent with an earlier theoretical study of Lommer et al. [38] of spin splitting in heterostructures, which predicted that in GaAs/AlGaAs QWs the Rashba term in the Hamiltonian is weak. In narrow-band semiconductors, however, Lommer et al. predict that the Rashba term becomes relevant. But this remains a not-yet-verified theoretical prediction. Another interesting study of the interface effects was done recently by Guettler et al. [39] following the calculations of Vervoort et al. [40]. Quantum well systems in which wells and barriers have different host atoms (so called "no-common-atom" heterostructures) were shown to have conduction electron spin relaxation enhanced by orders of magnitude compared to common-atom heterostructures. In particular, spin relaxation times in (InGa)As/InP QWs were found to be 20 (90) ps for electrons (holes), while the structures with common host atoms (InGa)As/(AsIn)As have spin relaxation times much longer: 600 (600) ps. This huge difference between otherwise similar samples is attributed to the large electric fields arising from the asymmetry at the interface (interface dipolar fields) [39].

Spin relaxation of conduction electrons can be controlled. This was first realized by Wagner et al. [41] who δ-doped GaAs/AlGaAs double heterostructures with Be (as acceptor). The measured spin relaxation time was about 20 ns which is *two* orders of magnitude longer than in similar homogeneously p-doped GaAs. The understanding of this finding is the following. The sample was heavily doped (8×10^{12} cm^{-2}) so the Bir-Aronov-Pikus mechanism was expected to dominate the relaxation. Photogenerated electrons, however, were spatially separated from holes which stayed mostly at the center of the GaAs layer, close to the Be dopants. There was, however, still enough overlap between electrons and the holes for efficient recombination so that the radiation polarization could be studied. The decrease of the overlap between electrons and holes reduced the efficiency of the Bir-Aronov-Pikus mechanism and increased T_1. This experiment can be also taken as a confirmation that the Aronov-Bir-Pikus mechanism is dominant in heavily p-doped heterostructures.

The next important step in controlling spin relaxation was the observation of a large enhancement of the spin memory of electrons in II-VI semiconductor QWs by Kikkawa et al. [42]. Introducing a (two dimensional) electron gas by n-doping the II-VI QWs was found to increase electronic spin memory by several orders of magnitude. The studied samples were modulation-doped $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$ quantum wells with electron densities 2×10^{11} and 5×10^{11} cm^{-2} (an additional insulating sample was used as a benchmark). Spin polarization was induced by a circularly polarized pump pulse directed normal to the sample surface. The spins, initially polarized normal, began to precess along an external magnetic field oriented along the surface plane. After a time δt, a probe pulse of a linearly polarized light detected the orientation of the spins. The major result of the study was that in doped samples electron spin remained polarized for almost three orders of magnitude longer than in the insulating (no Fermi see) sample. The measured T_1 was on the nanosecond scale, strongly dependent on the magnetic field and weakly dependent on temperature and mobility. Although the nanosecond time scales and the increase of the observed polarization in strong

magnetic fields (usually a Tesla) could be explained by the D'yakonov-Perel' mechanism [25], the temperature and mobility (in)dependence remain a puzzle. The overall increase of T_1 by donor doping can be understood in the following way [42]. In insulating samples photoexcited spin-polarized electrons quickly recombine with holes. This happens in picoseconds. In the presence of a Fermi sea photoexcited electrons do not recombine (there are plenty other electrons available for recombination) so they lose their spins in nanoseconds, which are natural time scales for spin relaxation. There is a caveat, however. The above scenario is true only if holes lose their spins faster than they recombine with electrons. Otherwise only electrons from the Fermi sea with a preferred spin would recombine, leaving behind a net opposite spin that counters that of the photoexcited electrons. The fast hole relaxation certainly happens in the bulk (and similar enhancement of T_1 has been observed in n-doped bulk GaAs by Kikkawa and Awschalom [43]), but not necessarily in quantum heterostructures [21–23]. This issue therefore remains open. Very recent optically pumped nuclear magnetic resonance measurements [44] in n-doped AlGaAs/GaAs multiple quantum well systems indicate unusually long $T_1 \gtrsim 100\mu$s at temperatures below 500 mK in the two-dimensional electron gas system under the application of a strong ($\gtrsim 12$ T) external magnetic field. It is unclear whether this remarkable decoupling (that is, $T_1 \gtrsim 100\mu$s) of the two-dimensional electron gas spins from its environment is an exotic feature of the fractional quantum Hall physics dominating the system, or is a more generic effect which could be controlled under less restrictive conditions.

It was recently demonstrated that spin polarized current can flow in a semiconductor. Hägele et al. [45] used a simple but ingenuous setup that consisted of a micrometer i-GaAs block attached to a p-modulation doped GaInAs QW layer. The free surface of the GaAs block was illuminated by a circularly polarized light. The photogenerated electrons then drifted towards the QW under the force of an applied electric field (photoexcited holes moved in the opposite direction towards the surface). The electrons recombined with holes upon hitting the QW, emitting light. By observing the polarization of the emitted light Hägele et al. concluded that electrons captured by the QW were polarized. The spin was almost completely conserved after the electrons traveled as long as 4 micrometers and under the fields up to 6 kV/cm, indicating very long spin diffusion lengths in these experiments [45].

IV. METALS

Only a dozen elemental metals have been investigated for spin relaxation so far. Early measurements of T_1 were done by the conduction electron spin resonance technique. This technique was demonstrated for metals by Griswold et al. [46], and Feher and Kip [47] used it to make the first T_1 measurement of Na, Be, and Li. This and subsequent measurements established that $1/T_1$ in metals depends strongly on the impurity content (especially in light metals like Li and Be) and grows linearly with temperature at high temperatures. Typical spin relaxation time scales were set to nanoseconds, although in very pure samples T_1 can reach microseconds at low temperatures (for example in sodium, as observed by Kolbe [48]). Reference [49] is a good source of these early spin relaxation measurements.

The next wave of measurements started with the realization of spin injection in metals. Suggested theoretically by Aronov [50], spin injection was first demonstrated in Al by John-

son and Silsbee [51]. Later measurements were done on Au [52] and Nb [53] films. The spin injection technique enables measurements of T_1 in virtually no magnetic fields so that T_1 can now be measured in superconductors, spin glasses, or Kondo systems where magnetic field qualitatively alters electronic states. Furthermore, by eliminating the need for magnetic fields to polarize electron spins one avoids complications like inhomogeneous line broadening, arising from g factor anisotropy. Johnson also succeeded in injecting spin polarized electrons into superconducting Nb films [53]. Spin relaxation of electrons (or, rather, quasiparticles) in superconductors is, however, poorly understood and the experiments, now done mostly on high-T_c materials [54,55] only manifest the lack of theoretical comprehension of the subject. Still waiting for its demonstration is spin injection into semiconductors. Although it was predicted long ago by Aronov and Pikus [56] it still remains a great experimental challenge.

The observations that $1/T_1 \sim T$ at high temperatures, the strong dependence on impurities, and characteristic nanosecond time scales has led to the general belief that conduction electrons in metals lose their spins by the Elliott-Yafet mechanism. Although simple estimates and even some analytical calculations were done for simplest metals like Na (Yafet [11]), careful numerical calculations are lacking. Experimental data are usually analyzed to see if the simple relation suggested by Yafet [11],

$$1/T_1 \sim b^2 \rho, \tag{1}$$

where ρ is resistivity, is obeyed. The spin-mixing b^2 is the fitting parameter so the temperature behavior of $1/T_1$ is determined solely by ρ. At high temperatures $1/T_1 \sim \rho \sim T$ as observed. At low temperatures the spin relaxation should obey the Yafet law $1/T_1 \sim T^5$ (in parallel to the Bloch law $\rho \sim T^5$), but so far this has not been observed, mainly due to the large contribution from impurity and boundary scattering. (Even after subtracting this temperature independent background the uncertainties of the measurements prevent a definite experimental conclusion about the low T behavior.)

Equation 1 suggests that dividing $1/T_1$ by b^2 one obtains resistivity, up to a multiplicative (material independent) constant. Resistivity, divided by its value ρ_D at T_D and expressed as function of reduced temperature T/T_D follows a simple Grüneisen curve, the same for all simple metals. Monod and Beuneu [49] applied this reasoning to then available experimental data of T_1. For the spin mixing b^2 they substituted values obtained from atomic parameters of the corresponding elements. The resulting (revised) scaling is reproduced in Fig. 2. (The original scaling [49] has Γ_s divided by b^2, not by $b^2 \rho_D$.) The picture is surprising. While some metals (the "main group") nicely follow a single Grüneisen curve, others do not. There seems to be no obvious reason for the observed behavior. Metals Na and Al, for example, are quite similar in that their atomic b^2 differ by less than 10% [49]. Yet the spin relaxation times at T_D are 0.1 ns for Al and 20 ns for Na [57].

The solution to this puzzle can be found by recognizing [57] that the main group is formed by *monovalent* alkali and noble metals, while the metals with underestimated b^2, Al, Pd, Mg, and Be are *polyvalent* (no other metals have been measured for T_1 in a wide enough temperature region). Monovalent metals have their Fermi surfaces inside Brillouin zone boundaries so that distance between neighboring bands, ΔE is quite uniform and of the order of the Fermi energy E_F. The spin mixing is then $b^2 \approx (\lambda/E_F)^2$ for all states on the Fermi surface. Polyvalent metals, on the other hand, have Fermi surfaces which cross Brillouin zone boundaries, and often also special symmetry points and accidental

degeneracy lines. When this happens the electron spin relaxation is significantly enhanced. This was first noted by Silsbee and Beuneu [58] who estimated the contribution to Al $1/T_1$ from accidental degeneracy lines. Later the present authors gave a rigorous and detailed treatment of how not only accidental degeneracy, but all the band anomalies contribute to $1/T_1$ [57]. This treatment led to the spin-hot-spot model [57] which explains why all the measured polyvalent metals have spin relaxation faster than expected from a naive theory. In addition to explaining experiment, the spin-hot-spot model predicts the behavior of other polyvalent metals. The model is illustrated in Fig. 3.

As an example, consider a metal whose Fermi surface crosses a single Brillouin zone boundary [57,59]. The distance between energy bands ΔE is about E_F for all Fermi surface states except those close to the boundary. There $\Delta E \approx 2V$ [14], where V is the Fourier component of the lattice potential associated with the boundary. Since in most cases $V \ll E_F$ the spin mixing $b^2 \approx (\lambda/V)^2$ is much larger than on average. If an electron jumps into such states, the chance that its spin will be flipped is much enhanced. Similarly if the electron jumps *from* these "spin hot spots." But how much the states with $\Delta E \approx 2V$ contribute to spin relaxation depends on how many they are relative to the number of states on the Fermi surface. A single electron experiences thousands of jumps due to momentum scattering before its spin flips. Therefore the spin relaxation rate $1/T_1$ is determined by the average $\langle b^2 \rangle$ of b^2 over the Fermi surface. The majority of states with $\Delta E \approx E_F$ contribute $(\lambda/E_F)^2 \times 1$ (the value of b^2 times the probability of occurrence, which in this case is close to one) to $\langle b^2 \rangle$. The probability of finding a state with $\Delta E \approx 2V$ on the Fermi surface turns out to be about V/E_F [59], so the spin hot spots contribute about $(\lambda/V)^2 \times (V/E_F)$, which is $(\lambda/E_F)^2 \times (E_F/V)$. This is larger by E_F/V than the contribution from ordinary states. Typically $E_F/V \approx 10$, and considering that in reality the Fermi surface crosses more than one Brillouin zone boundary, the spin relaxation can be enhanced up to two orders of magnitude. Electron jumps that include at least one spin-hot-spot state dominate spin relaxation to the extent that the majority of scattering events (those outside the spin hot spots) can be neglected.

The spin-hot-spot picture not only solves a long-standing experimental puzzle, but also shows a way to tailor the spin relaxation of electrons in a conduction band. Spin relaxation of a monovalent metal, for example, can be enhanced by alloying with a polyvalent metal. This brings more electrons into the conduction band. As the Fermi surface increases, it begins to cross Brillouin zone boundaries and other spin-hot-spot regions. The enhancement of $1/T_1$ can be significant. Similarly, $1/T_1$ can be reduced by orders of magnitude by alloying polyvalent metals with monovalent. Applying pressure, reducing the dimensionality, or doping into a semiconductor conduction bands as well as any other method of modifying the band structure should work. The rule of thumb for reducing $1/T_1$ is washing the spin hot spots off the Fermi surface. (Another possibility would be to inhibit scattering in or out the spin hot spots, but this is hardly realizable.)

The most important work ahead is to catalog $1/T_1$ for more metallic elements and alloys. So far only the simplest metals have been carefully studied over large enough temperature ranges, but even in these cases it is not clear, for example, as to how phonon-induced $1/T_1$ behaves at low temperatures. It is plausible that understanding $1/T_1$ in the transition metals will require new insights (such as establishing the role of the *s-d* exchange). Another exciting possibility is that the measurements at high enough temperatures will settle the question of

the so called "resistivity saturation" [60] which occurs in many transition metals. Indeed, the two competing models of this phenomenon imply different scenarios for $1/T_1$: the "phonon ineffectiveness" model [61] implies saturation of $1/T_1$, while the model emphasizing the role of quantum corrections to Boltzmann theory [62] apparently does not [63]. Finally, theory should yield probabilities of various spin-flip processes in different metals. Empirical pseudopotential and density functional techniques seem quite adequate to perform such calculations. Some work in this direction is already under way [64].

V. CONCLUSION

We have provided a brief informal review of the current understanding of spin relaxation phenomenon in metals and semiconductors. Although studying spin relaxation through electron spin resonance measurements and developing its microscopic understanding through quantitative band structure analyses were among the more active early research areas in solid state physics (dating back to the early 1950s), it is surprising that our current understanding of the phenomenon is quite incomplete and is restricted mostly to bulk elemental metals and some of the III-V semiconductor materials (both bulk and quantum well systems). There is a great deal of renewed current interest in the subject because of the potential spintronics applications offering the highly desirable possibility of monolithic integration of electronic, magnetic, and optical devices in single chips as well as the exciting prospect of using spin as a quantum bit in proposed quantum computer architectures. It should, however, be emphasized that all of these proposed applications necessarily require comprehensive quantitative understanding of physical processes controlling spin coherence in electronic materials. In particular, there is an acute need to develop techniques which can manipulate spin dynamics in a controlled coherent way which necessitates having long spin relaxation times and/or spin diffusion lengths. Our understanding of spin coherence in small mesoscopic systems and more importantly, at or across interfaces (metal/semiconductor, semiconductor/semiconductor) is currently rudimentary to non-existent. Much work (both theoretical and experimental as well as materials and fabrication related) is needed to develop a comprehensive understanding of spin coherence in electronic materials before the spintronics dream can become a viable reality.

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FIGURES

FIG. 1. The relevant spin relaxation mechanisms for conduction electrons. (A) *The Elliott-Yafet mechanism.* The periodic spin-orbit interaction makes the spin "up" Bloch states contain small spin down amplitude, and vice versa. Impurities, boundaries, and phonons can induce transitions between spin "up" and "down" leading to spin degradation. (B) *The D'yakonov-Perel' mechanism.* In noncentrosymmetric crystals spin bands are no longer degenerate: in the same momentum state spin up has different energy than spin down. This is equivalent to having internal magnetic fields, one for each momentum. The spin of an electron precesses along such a field, until the electron momentum changes by impurity, boundary, or phonon scattering. Then the precession starts again, but along a different axis. Since the spin polarization changes during the precession, the scattering acts against the spin relaxation. (C) *The Bir-Aronov-Pikus mechanism.* The exchange interaction between electrons and holes causes the electron spins to precess along some effective magnetic field determined by hole spins. In the limit of strong hole spin relaxation, this effective field randomly changes before the full precession is completed, reducing the electron spin relaxation.

FIG. 2. Revised Monod-Beuneu scaling. The measured width $\Gamma_s = const \times (1/T_1)$ of the conduction electron spin resonance signal is divided by the effective spin-mixing probability b^2 obtained from atomic parameters, and by resistivity ρ_D at Debye temperature T_D. This should follow a Grüneisen curve when plotted as function of reduced temperature T/T_D. The alkali metals fall onto a single curve while Al, Pd, Be, and Mg do not, indicating that their b^2 is much larger than estimated from atomic parameters.

FIG. 3. The spin-hot-spot model. (A) *Monovalent metals.* As electrons scatter and change momentum, they perform a random walk on the Fermi surface. At each jump the electrons have a small chance of flipping their spin (the Elliott-Yafet mechanism), indicated on the right. In monovalent metals this chance is uniform over the Fermi surface and is roughly equal to $(\lambda/E_F)^2$. (B) *Polyvalent metals.* Fermi surfaces of polyvalent metals contain spin hot spots (black stains), which are states at Brillouin zone boundaries, special symmetry points, or accidental degeneracy lines. If an electron jumps into such a state, its chance of flipping spin is much enhanced. Although spin hot spots form a small part of the Fermi surface and the probability that an electron jumps there is quite small, they nevertheless dominate the electron spin relaxation.

A

B